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6. AUTHORS Pulickel M. Ajayan			5d. PROJECT NUMBER		
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14. ABSTRACT The work was designed towards creating aligned multiwalled carbon nanotube arrays by chemical vapor deposition (CVD) of xylene hydrocarbon precursor and simultaneous vapor phase delivery of catalyst particles. Low density nanotube arrays as well as highly dense pyrolytic carbon coated nanotube arrays were produced. The nanotube arrays could be grown to several hundreds of microns long. The simultaneous growth of nanotubes and densification of the aligned carbon nanotube (ACNT) films by carbon infiltration in the interstitial spaces between nanotubes were accomplished in a single step by the combination of the chemical vapor deposition and chemical vapor infiltration processes. Analysis showed that after infiltration, the					
15. SUBJECT TERMS carbon nanotubes, composite, thermal, mechanical, chemical vapor deposition					
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a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER 713-348-5904

## Report Title

### Carbon Nanotube Arrays for Thermal Management Applications

#### ABSTRACT

The work was designed towards creating aligned multiwalled carbon nanotube arrays by chemical vapor deposition (CVD) of xylene hydrocarbon precursor and simultaneous vapor phase delivery of catalyst particles. Low density nanotube arrays as well as highly dense pyrolytic carbon coated nanotube arrays were produced. The nanotube arrays could be grown to several hundreds of microns long. The simultaneous growth of nanotubes and densification of the aligned carbon nanotube (ACNT) films by carbon infiltration in the interstitial spaces between nanotubes were accomplished in a single step by the combination of the chemical vapor deposition and chemical vapor infiltration processes. Analysis showed that after infiltration, the diameters of nanotubes and bulk density of the nanotube films were increased by an order of magnitude (and hence the porosity of the nanotube films is decreased). During the densification, the individual nanotubes becomes coated with disordered graphitized carbon, as evidenced in structural characterization. The compressive modulus of the densified films was increased by three orders of magnitude during densification. Electrical properties also showed marked differences between the low density and densified films. The densified nanotube films could be seen as a new form of carbon-carbon nanocomposite and could find applications as multifunctional nanocomposites.

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#### List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

##### (a) Papers published in peer-reviewed journals (N/A for none)

1. Xuesong Li, Lijie Ci, Swastik Kar, Caterina Soldano, Stephen J. Kilpatrick and Pulickel M. Ajayan, Densified aligned carbon nanotube films via vapor phase infiltration of carbon, Carbon, 45, 847 (2007).

Number of Papers published in peer-reviewed journals: 1.00

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##### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

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##### (c) Presentations

1. "Engineering of Carbon Nanotube Architectures", Missouri Nanoalliance Meeting, University of Missouri, Columbia, MO (October 7, 2006). (Keynote Lecture)
2. "Engineering of Carbon Nanotube Architectures", Workshop on Carbon Technologies, Pennsylvania State University, State College, PA (October 16, 2006).
3. "Engineering of Carbon Nanotube Architectures", Kavli US-Chinese National Academy of Science Meeting, Irvine, CA (October 27, 2006).
4. "Engineering of Carbon Nanotubes" Gordon Research Conference on Chemistry of Hydrocarbon Resources, Venture, CA (January 9, 2007).
5. "Engineering of Carbon Nanotubes" Special seminar, Applied Materials, San Jose, CA (January 11, 2007).
6. "Carbon Nanotube Growth: Understanding or Lack of", Singlewalled Nanotube Growth Workshop, Canyon of the Eagles, Texas (April 17, 2007).
7. "Carbon Nanotubes – Related Technologies and Engineering Concepts", Seminar, Air Force Research Labs, Dayton, OH (April 20, 2007).
8. "Engineering Carbon Nanotube Architectures", Nanotechnology Symposium, Polytechnic University of Brooklyn, Brooklyn, NY (April 23, 2007).
9. "Engineering Carbon Nanotube Architectures", Nanotube 07, Ouro Preto, Brazil (June 25, 2007).
10. "Carbon Nanotube Architectures for Applications", Nanotech Briefs Conference, Boston, MA (November 14, 2007).

Number of Presentations: 10.00

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#### Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

0

(d) Manuscripts

Number of Manuscripts:

0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Salomeh Tabatabaei	0.20
FTE Equivalent:	0.20
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Maneesh Amin	0.25
FTE Equivalent:	0.25
Total Number:	1

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

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### Names of Personnel receiving masters degrees

NAME

Total Number:

### Names of personnel receiving PhDs

NAME

Total Number:

### Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

### Sub Contractors (DD882)

### Inventions (DD882)



# **FINAL REPORT**

## **Title: Carbon Nanotube Arrays for Thermal Management Applications**

Award Number: W911NF-06-1-0108

Principal Investigator: Pulickel M. Ajayan (Rensselaer Polytechnic Institute)

### **1. Statement of the Problem Studied**

The project's primary goal was to grow carbon nanotube arrays of varying density on a variety of substrates, characterize them structurally and thermally. The fundamental understanding of the growth mechanism of vertically aligned nanotube array growth on substrates would also be investigated. The thermal characterization of these arrays of nanotubes was proposed through a collaborative effort with the Army Research Laboratory (ARL).

### **2. Summary of Most Important Results**

#### **Abstract**

The work was designed towards creating aligned multiwalled carbon nanotube arrays by chemical vapor deposition (CVD) of xylene hydrocarbon precursor and simultaneous vapor phase delivery of catalyst particles. Low density nanotube arrays as well as highly dense pyrolytic carbon coated nanotube arrays were produced. The nanotube arrays could be grown to several hundreds of microns long. The simultaneous growth of nanotubes and densification of the aligned carbon nanotube (ACNT) films by carbon infiltration in the interstitial spaces between nanotubes were accomplished in a single step by the combination of the chemical vapor deposition and chemical vapor infiltration processes. Analysis showed that after infiltration, the diameters of nanotubes and bulk density of the nanotube films were increased by an order of magnitude (and hence the porosity of the nanotube films is decreased). During the densification, the individual nanotubes becomes coated with disordered graphitized carbon, as evidenced in structural characterization. The compressive modulus of the densified films was increased by three orders of magnitude during densification. Electrical properties also showed marked differences between the low density and densified films. The densified nanotube films could be seen as a new form of carbon-carbon nanocomposite and could find applications as multifunctional nanocomposites.

#### **2.1. Growth and Density Control of Vertically Aligned Carbon Nanotubes on Substrates**

We have been working on CVD of nanotubes on substrates for nearly a decade. Our lab initiated the process of growing vertically aligned nanotubes on various substrates using a unique vapor phase catalyst delivery technique where the entire substrate is simultaneously exposed to vapors containing both the hydrocarbon and metal catalyst. The metal catalyst is delivered through a

metallorganic precursor (ferrocene) which is pyrolyzed along with the hydrocarbon and hence catalyzes the growth of nanotubes. The growth can also be selective since growth rate becomes significantly different depending on the substrate surface chemistry and interaction of the catalyst particles with the substrate. The growth rate of nanotubes levels off typically after a certain amount of time and the vertically aligned arrays get shunted in growth length after this time. Routinely few hundred microns of nanotube lengths can be grown by this approach. The films of nanotubes so deposited (figure 1) have extremely low density with only less than 10% filling fraction of nanotubes in the entire film volume. This means that there is a lot of empty space between the nanotubes in these arrays but yet the nanotube film is held together from van der Waals forces that exist between individual nanotubes in the films. Long time CVD does not increase the length of nanotubes in the films but the film gets densified as the carbon deposits as pyrolytic graphitized carbon depositing around the original nanotubes in the spaces between them. By this method the density of the carbon nanotube films can be increased by nearly an order of magnitude and it can be controlled by controlling the CVD time.

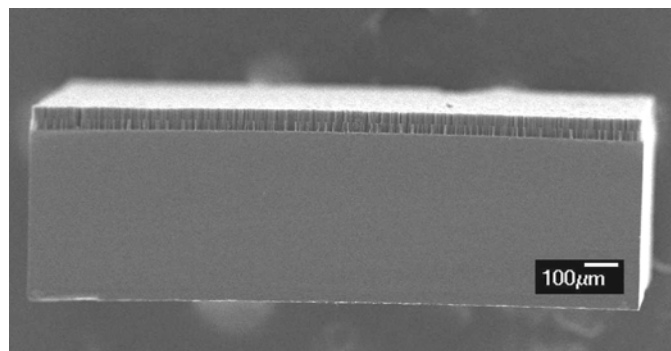


Figure 1: A uniform film of multiwalled nanotubes deposited on a quartz substrate by the chemical vapor deposition of xylene-ferrocene mixture at about 750 degrees Celsius.

## 2.2. Aligned CNT arrays of Varying Densities

Figure 2 shows the various stages of the growth of thin MWNT in the vertically direction and the subsequent thickening of the nanotubes with further infiltration and CVD of graphitized carbon. The structural differences between the nanotube core and pyrolyzed carbon shell suggest two distinct processes for short-time growth and long-time growth.

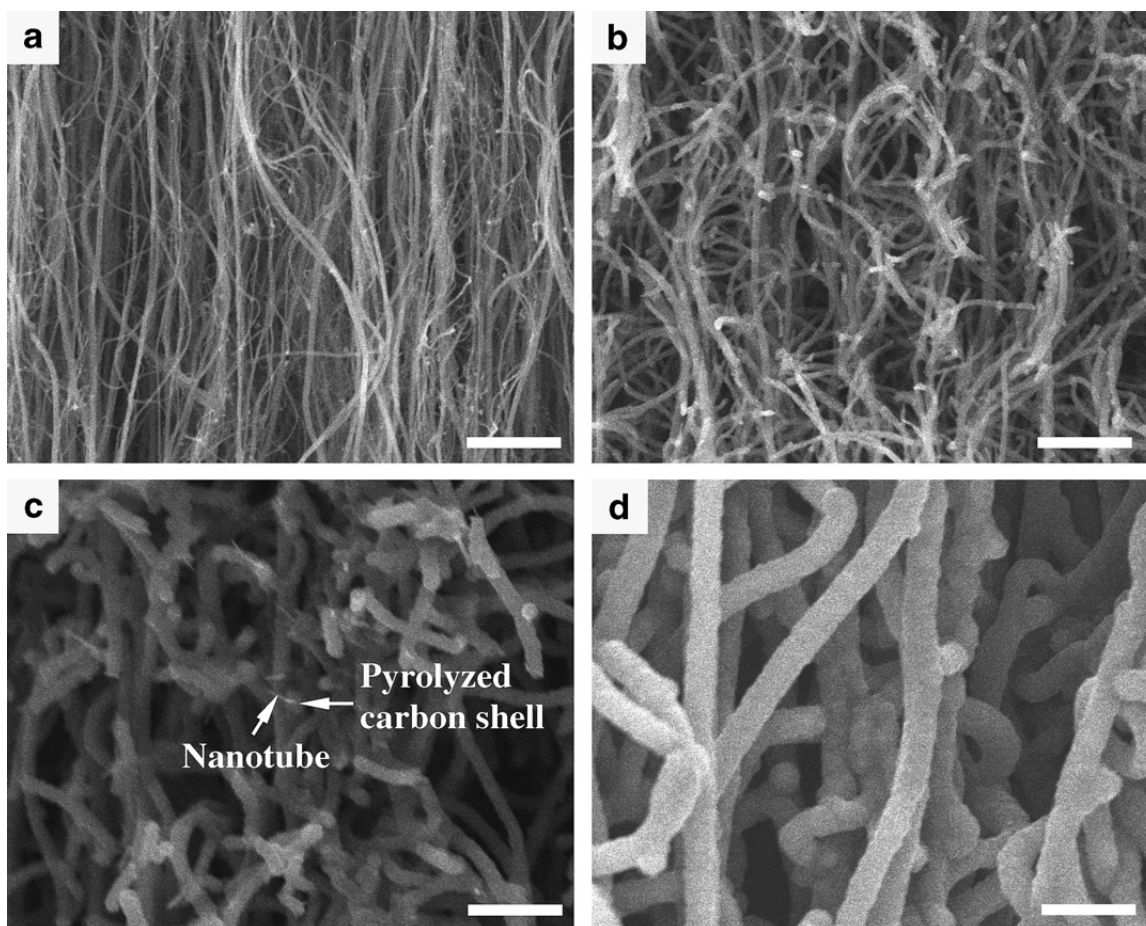


Figure 2: SEM images of nanotubes with different growth times: (a) 30 min, (b) 120 min, (c) 300 min, and (d) 600 min, respectively. Nanotubes were thickened by the deposition of pyrolyzed carbon when the growth time was elongated. Scale bars: 1 micron. (taken from reference 1)

This kinetics of the deposition process is more clearly shown by the plots of ACNT film thickness and average nanotube diameter vs. growth time (fig. 3), in which, there are three distinct regions. In Region I, or the nanotube growth region, the catalyst particles kept their activity and nanotubes kept growing at constant rate. In Region II, noted as the transition region, the growth rate of nanotubes decreases, as the carbon infiltration process starts. In Region III, or the infiltration region, the growth of nanotubes is terminated due to complete loss of catalyst activity. Instead, more and more pyrolyzed carbon gets coated on the nanotubes. An obvious result of this infiltration process is the increase in the bulk density, and hence the decrease in the porosity of the ACNT film (Fig. 3b). The bulk density of the ACNT film for short time growth is  $\sim 0.07 \text{ g/cm}^3$ , while that for long term growth is  $1.38 \text{ g/cm}^3$ , an increase of about a factor of 20, and as a result, the porosity decreases from 90-95% to 30-40%, showing effective infiltration of carbon, into the interstices between vertically aligned individual nanotubes in the film, as conformal pyrolyzed carbon coating on the nanotubes.



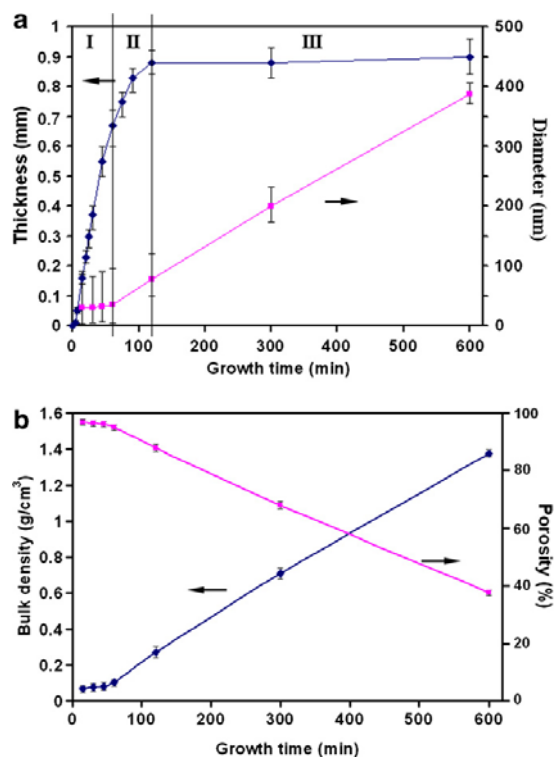


Figure 3: ACNT film thickness and average nanotube diameter vs. growth time. The ACNT film thickness kept increasing during the first 2 h and then stopped, no matter how the growth time was elongated. In contrast, the nanotube diameter changed little at the beginning of the growth and then increased with growth time, caused by the deposition of pyrolyzed carbon. (b) The bulk density and porosity of ACNT film vs. growth time. The bulk density of ACNT film was increased and the porosity of ACNT film was decreased when the growth time was increased due to the infiltration of pyrolyzed carbon. (taken from reference 1)

### 2.3. Air Assisted CVD to Produce Super-long CNT arrays

The challenge in growing very long nanotubes and hence thick films of ACNT is in keeping the catalyst particles during long periods of time without the catalyst getting encapsulated with graphitized carbon. There have been previous attempts in doing this and one approach that has yielded fair amount of success is by introducing small amounts of water vapor in the CVD process. The water vapor removes the carbon coating and keeps the catalyst nanoparticle active for long periods. Following these approaches, we modified our CVD by introducing small amount of air in the process, which essentially accomplishes the same goal as water vapor. Preliminary results suggested that this is a very effective process and we were able to grow extremely long nanotubes that are over 1 cm in length (figure 4).

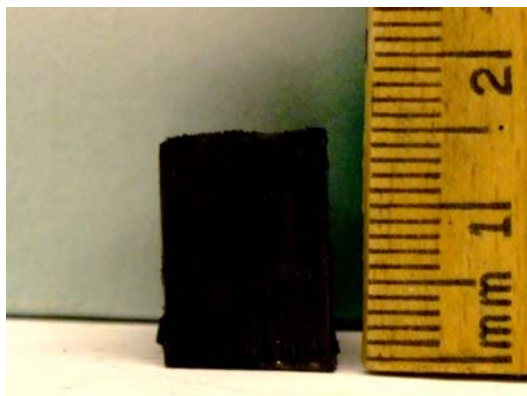


Figure 4: Super long nanotubes grown using CVD of ferrocene and xylene after adding small concentration of air into the process. The ACNT grown here is also very low density and has not been infiltrated with graphitized carbon.

### **Conclusions and Ongoing Work**

The work enabled us to understand the kinetics of the growth of ACNT arrays and ways to control the density of the nanotube films. A densified nanotube based carbon composite film was thus developed. Due to the increase in density of the films, it is expected that it will have interesting mechanical and thermal properties. We are continuing our collaborations with ARL to get thermal properties measured from the composite structures we have created. Also, by slightly modifying the CVD process we are able to make super long nanotubes. The structural, electrical and thermal characterization of these super long nanotubes are in progress.

### **3. Publications and Presentations**

*Journal publication:*

1. Xuesong Li, Lijie Ci, Swastik Kar, Caterina Soldano, Stephen J. Kilpatrick and Pulickel M. Ajayan, Densified aligned carbon nanotube films via vapor phase infiltration of carbon, *Carbon*, 45, 847 (2007).

*Select invited talks by the PI at Conferences (Pulickel M. Ajayan):*

1. "Engineering of Carbon Nanotube Architectures", Missouri Nanoalliance Meeting, University of Missouri, Columbia, MO (October 7, 2006).
2. "Engineering of Carbon Nanotube Architectures", Workshop on Carbon Technologies, Pennsylvania State University, State College, PA (October 16, 2006).
3. "Engineering of Carbon Nanotube Architectures", Kavli US-Chinese National Academy of Science Meeting, Irvine, CA (October 27, 2006).
4. "Engineering of Carbon Nanotubes" Gordon Research Conference on Chemistry of Hydrocarbon Resources, Venture, CA (January 9, 2007).

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10. "Carbon Nanotube Architectures for Applications", Nanotech Briefs Conference, Boston, MA (November 14, 2007).

#### **4. Personnel and Collaboration with DoD Laboratory**

The project was directed by the PI, Prof. Pulckel M. Ajayan. Funding was small, so no full time student/post-docs could be supported by the fund. However, facilities and personnel working as part of the National Science Foundation funded Nanoscale Science and Engineering Center (NSEC) and the New York Focus Center for Interconnects, were leveraged and contributed to the project.

A strong collaboration was established between the Army Research Laboratories, between Dr. Stephen Kilpatrick. The collaboration involved exchange of specimens, discussions, visits and joint publication. Some of the future publications that will come out of the initial results obtained as part of the project will involve personnel from both institutions. The future planned work, in the area of thermal measurements of the nanotube arrays that have been grown, will also be based on collaboration between the PI institution and ARL. The PI has recently moved from RPI to Rice University (Houston, Texas).